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GUANIDINE-FUNCTIONALIZED MAGNETIC Fe_3O_4 NANOPARTICLES AS A NEW SORBENT FOR PRECONCENTRATION OF HEAVY METAL IONS IN WATER SAMPLES

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Fe_3O_4 functionalized guanidine , a new adsorbent for determination of Pb, Cd, Zn and Cu by flame atomic absorption spectrometry was synthesized and characterized with different techniques. In this work, the effect of various parameters such as the pH, the type and volume of eluent, sample volume and interfering ions were optimized. After optimizing the experimental conditions, a linear calibration graph was obtained for determination of Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II}. The linear ranges were found to be 14-550 μg L^{-1}, 3 – 90 μg L^{-1}, 19 – 200 μg L^{-1} and 40-600 μg L^{-1} for Copper, Cadmium, Zinc, and Lead, respectively. The limits of detection were 4.78, 1.08, 7.6, and 11.8 μg L^{-1} for Copper, Cadmium, Zinc, and Lead, respectively. The relative standard deviation for ten replicate determinations of Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II} were 3, 2.1, 2.9 and 1.2 respectively. The maximum capacity of the adsorbent was found to be 15.2 (±1.7) mg, 19.70 (±0.7) mg, 12.20 (±0.9) mg and 13.60 (±0.8) mg of Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II} per g functionalized magnetic nanoparticle, respectively. Applicability of the method was evaluated by analyzing trace amounts of Copper, Cadmium, Zinc, and Lead in different water samples.

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Keywords: Magnetic solid phase extraction; Lead(II); Copper(II); Zinc(II); Cadmium(II)

1. Introduction

Heavy metals have been extremely released into the environment due to rapid industrialization and have created adverse health effects in human metabolism. The present obvious concerns are due to their persistence in the environment and documented potential for serious health consequences. Cu, Zn, Cd, Hg, Pb and Ni are considered most heavy metals in aquatic systems. Many metals including Fe (hemoglobin), Cu (respiratory pigments), Zn (enzymes), Co (vitamin B_{12}), Mo and Mn (enzyme) are, if in the appropriate concentrations, essential to living organisms but toxic at high concentrations. Some metals such as Sn, Ni, Se, Cr and As - that are not needed for metabolic activity - are toxic at quite low concentrations [1]. Therefore, determination of trace amounts of heavy metals in environmental samples is very important for analytical chemists. Several analytical techniques, such as flame atomic-absorption spectrometry (FAAS), inductively coupled plasma atomic emission spectrometry (ICP-AES) and inductively coupled plasma mass spectrometry (ICP-MS) are available for the determination of trace metals with sufficient sensitivity for most applications. Among these methods, FAAS, due to its simplicity and its lower price is more common than other instruments. But this technique has no sufficient sensitivity in direct determination of metals, therefore, separation and preconcentration methods is critical to obtaining efficient recovery. However, direct determination of metal ions of trace level is usually very limited due to their low level of concentration and matrix interferences [2].

There are many methods of preconcentration and separation, such as liquid liquid extraction (LLE) [3], ion-exchange techniques [4], coprecipitation [5], sorption on the various adsorbents, such as activated carbon [6], magnetic nanoparticle supported ephedrine [7] and other sorbent [8].

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Among them, SPEs are widely employed due to their simplicity, high concentration factor and low consumption of harmful organic solvents [9,10].

Compared with micrometer-sized particles used in the SPE, the magnetic nanoparticles (MNPs) offer a multitude of advantages that make them a better choice [11,12].

They have very high surface area-to-volume ratio and a short diffusion path, resulting in higher extraction capacity; rapid dynamics of extraction and higher extraction efficiencies [3-17]. But the main problem in practical use of nanoparticles is separation of them from large sample volumes without analyte loss. Therefore, a high speed centrifugation is inevitable, that may lead to unwanted results such as coprecipitation of interferents and/or loss of some target analytes. In past decades, separation technology based on functionalized magnetic nanoparticle (MNPs) has become a powerful complement to batch and column SPE.

In addition, by using superparamagnetic NPs such as Fe_3O_4, due to the magnetically assisted separation of these particles from the sample solution, a shorter analysis time can be achieved. These nanoparticle are attracted to a magnetic field. However when the field is removed, no residual magnetism remained. Because of these properties, nanoparticles are suitable for sample preparation in comparison with non-magnetic adsorbents, no needing centrifuging or filtration of the sample after extraction [18-22].

The aim of the present study was to develop a NP-based method for the preconcentration and determination of trace amounts of Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II}. The method is based on the extraction of cations as hydrophobic complexes of cation - guanidine on guanidine – coated Fe_3O_4 NPs. The amounts of Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II} in extracted phase were determined by FAAS. In the best of our knowledge, this adsorbent has not been used to the separation and preconcentration of trace amount of metal ions.

2. Experimental

2.1 Reagents and solutions

(3-chlorooproypyl)-trimethoxysilane(CPTMS), all acids and organic solvents, stock standard solutions of Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II} (1000 mg L^{-1}) and analytical grade nitrate salts of other metal ions were purchased from Merck and were used without more purification.

Doubly distilled deionized water was used throughout. The Working standard solutions were prepared by appropriate dilution of the stock standard solutions with doubly distilled water.

2.2 Apparatus

A shimadzu model AA-670 atomic absorption spectrometer equipped with Lead, Cadmium, Zinc and Copper hollow cathode lamps and air-acetylene flame was used for determination of the metal ions. All pH settings were carried out by a Metrohm E-691 digital pH meter with a combined glass electrode. The infrared spectra were recorded using an infrared spectrometer (Bruker-Vector 22) with KBr disks in the range of 4000-400 cm^{-1}. The scanning electron microscopy (SEM) image was obtained by VEGA TESCAN. The X-ray powder diffraction (XRD) were collected on an X'Pert MPD Philips diffractometer with Cu Ka radiation source (λ= 1.54050 Å) at 40 kV voltage and 40 mA current. The thermogravimetric analysis (TGA) was carried out on a Bähr STA 503 instrument (Germany) under air atmosphere, heating rate 10 $^{\circ}C$ min^{-1}. The magnetic measurements were carried out in a vibrating sample magnetometer (VSM, BHV-55, Riken, Japan) at room temperature. A magnet (Nd-Fe-B, 1.2 T, 50 × 40 × 20 mm) was used for magnetic separation. The elemental analysis (EA) was carried out with a CHNS-O Elemental Vario EL III, Elementar, Hanau-Germany.

2.3 Preparation of large-scale the magnetic Fe_3O_4 nanoparticles (MNPs)

$FeCl_3 \cdot 6H_2O$ (4.865 g, 0.018 mol) and $FeCl_2 \cdot 4H_2O$ (1.789 g, 0.0089 mol) were added to deionized water (100 mL) and sonicated until the salts dissolved completely. Then, 10 mL of 25% NH_4OH was added quickly into the reaction mixture in one portion under N_2 atmosphere at room temperature followed by stirring about 30 min with mechanical stirrer. The black precipitate was washed five times by using doubly distilled water [7].

2.4 Preparation of MNPs coated by (3-chlooropropyl)-trimethoxysilane (MNPs-CPTMS)

The obtained MNPs powder (1.5 g, 6.5 mmol) was dispersed in 250 mL ethanol/water (volume ratio, 1:1) solution by sonication for 30 min, and then CPTMS (99%, 2.5 g, 12.6 mmol) was added to the mixture. After mechanical stirring under N_2 atmosphere at 33-38 °C for 8 h, the suspended substance was separated with centrifugation (RCF = 13, 200×g for 30 min). The settled product was re-dispersed in ethanol by sonication. The final sample was separated by an external magnet and washed five times with ethanol. The product stored in a refrigerator to use [23].

2.5 Preparation of guanidine-functionalized magnetic Fe_3O_4 nanoparticles (MNPs- Guanidine)

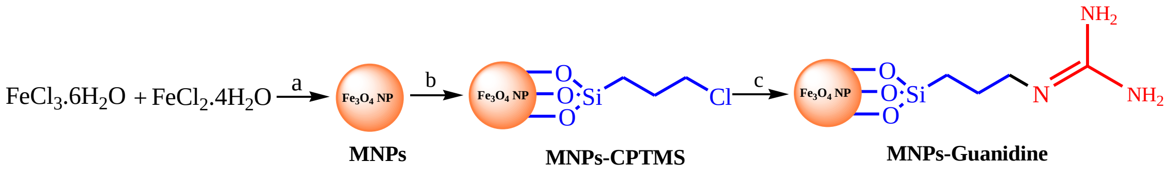
The MNPs-CPTMS (1.000 g) was dispersed in dry toluene (6.0-8.0 mL) by ultrasonic bath for 10 min. Subsequently, guanidine hydrochloride (0.382 g, 0.004 mmol) and sodium bicarbonate (0.672 g, 0.008 mmol) were added and the mixture was refluxed for 28 h. Then, the final product was separated by magnetic decantation and washed twice by dry CH_2Cl_2, EtOH and CH_2Cl_2, respectively to remove the unattached substrates. The product was stored in a refrigerator to use.

2.6. The general procedure for extraction of ions by the functionalized nanoparticle

An aqueous solution (50.0 mL) containing 10.0 µg Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II} was prepared and pH was adjusted at 6.0. The solution was added to 10.0 mg adsorbent in beaker. The sample solution was sonicated for 10 min to simplify adsorption of Lead, Zinc, Cadmium and Copper ions. Then, a strong magnet was used and the magnetic adsorbent separated after a few minutes and the supernatants were decanted. For elution adsorbed analyte ions from nanoparticles, 4.0 mL EDTA (0.5 mol L^{-1}) was added and the solution was again sonicated for 5 min and exposed on the magnet to deposit the magnetic nanoparticles. Afterwards, the eluate containing metal ions was determined by FAAS

2.7 Synthesis and Characterization of Magnetic nanoparticles supported guanidine (MNPs-Guanidine)

The process of the preparation guanidine-functionalized magnetic Fe_3O_4 nanoparticles is shown in Scheme 1.



Scheme 1. (a) Aqueous ammonia, N_2, rt, 30 min; (b) (3-chlooropropyl)-trimethoxysilane, ethanol/water, 40 ℃, 8 h; (c) guanidine hydrochloride, $NaHCO_3$, dry toluene, reflux, 28 h.

MNPs-Guanidine was characterized using a variety of different techniques including XRD, SEM, TGA, EDX, FT-IR, EA and vibrating sample magnetometer (VSM). The position and relative intensities of all peaks in the XRD pattern of MNPs–Guanidine confirm well with standard XRD pattern of Fe_3O_4, indicating retention of the crystalline cubic spinel structure during functionalization of MNPs (Figure S1. in Electronic supplementary information).

The SEM image of MNPs-Guanidine was confirmed that it was made up of uniform nanometer sized particles less than 17 nm (FigureS2. in Electronic supplementary information).

The TGA was used to determine the percent of organic functional groups chemisorbed onto the surface of magnetic nanoparticle. The TGA curve of the MNPs-Guanidine shows a weight loss about 10% from 260 to 600 °C, resulting from the decomposition of organic materials grafting to the MNPs surface (FigureS3. in Electronic supplementary information). On the basis of this result, the well grafting of guanidinyl propyl groups on the MNPs is verified.

EDX spectrum shows the elemental composition (N, Si and Fe) of the MNPs-Guanidine (Figure S4 in Electronic supplementary information).Successful functionalization of the MNPs can be inferred from FT-IR techniques. The FTIR spectrum (Figure1) of MNPs–Guanidine shows peaks (1443 and 3381 cm^{-1} bands corresponding to the C-N and N-H stretches, respectively) that are characteristic of a functionalized guanidine group, which clearly differs from that of the unfunctionalized Fe_3O_4 nanomagnets (MNPs) and 3-chloropropylsilica-functionalized magnetic nanoparticles (MNPs-CPTMS).

Elemental analysis results showed that the carbon, hydrogen, and nitrogen content of the MNPs-Guanidine was 5.7, 0.5, and 0.9 (wt%), respectively. The loading of the guanidine function on the magnetic nanoparticles was determined by elemental analysis of nitrogen as 0.22 mmol g^{-1} (FigureS4. in Electronic supplementary information).

Magnetization curve measured at room temperature showed that MNPs-Guanidine is superparamagnetic. As expected, the saturation magnetization (Ms) value of MNPs-Guanidine compared to the bare MNPs is decreased due to the silica coating and the layer of the grafted catalyst. As a result, the modified MNPs have a typical superparamagnetic behavior and can be efficiently attracted with a small magnet.

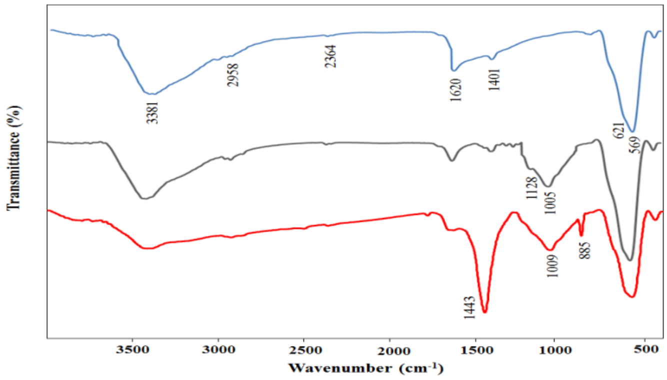


Fig. 1. FTIR spectra of MNPs (blue), MNPs-CPTMS (black) and MNPs-Guanidin (red)

3. Results and discussion

3.1 Effect of pH on the extraction

The existence of electron donating nitrogen atoms in structure of guanidine increases the stability of its transition and heavy metal ions complexes over other metal ions, especially alkali and alkaline earth cations [10,24]. On the other hand, guanidine is a base, thus the extraction of metal ions is highly dependent on the pH of the medium. Thus, the pH of aqueous samples was investigated in the pH range of 2.0 - 9.0 (using 1.0 mol L^{-1} of either nitric acid or sodium hydroxide solution). The results are shown in Figure2. As can be seen from Figure.2, in acidic solutions (pHs 2.0 – 3.0) the percent of extraction is low, that is due to protonation of nitrogen atoms of the guanidine at this pH range and in basic solution, may be due to formation of metal hydroxide species such as $Pb(OH)^+$, $Pb(OH)_2$, $Pb(OH)_3^-$ and $Cu_2(OH)_2^{2+}$, $Cu(OH)_2$, $Cu(OH)_3^-$, $Cu(OH)_4^{2-}$ and $Zn(OH)_2$, $Zn(OH)^+$ and $Cd(OH)_2$ [30,31,32,33] that leads to the decrease in the efficiency of extraction reduce in the stability of the complexes. But in the pH 6.0 the percent of extraction increased for all metal ions. Therefore, pH 6.0 was chosen for the further studies.

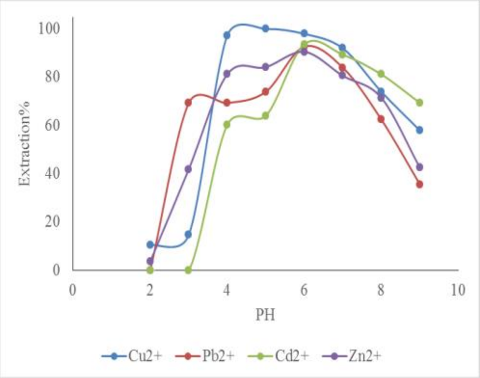


Fig. 2. Effect of pH on the recovery of 200 μg L^{-1} of Pb^{II}, Cd^{II}, Zn^{II} and Cu^{II} Conditions: amount of adsorbent, 10.0 mg; sample volume, 50.0 mL; eluent, 4.0 mL of EDTA(0.5 mol L^{-1}), extraction time, 10 min (n=3)

3.2 Selection of eluent type and volume

Metal-ions complexes extracted can be desorbed by using various types of eluents.In this work, EDTA(0.05-0.5 mol L-1), HNO3(0.1 mol L-1), H2SO4(0.1 mol L-1) and HCl(0.1 mol L-1) were used as eluent. The results shown in Figure3 confirm that the EDTA had a relative preference over other eluents. This is due to strong complexation ability of EDTA compared to guanidine groups. Thus, EDTA was chosen for further studies.

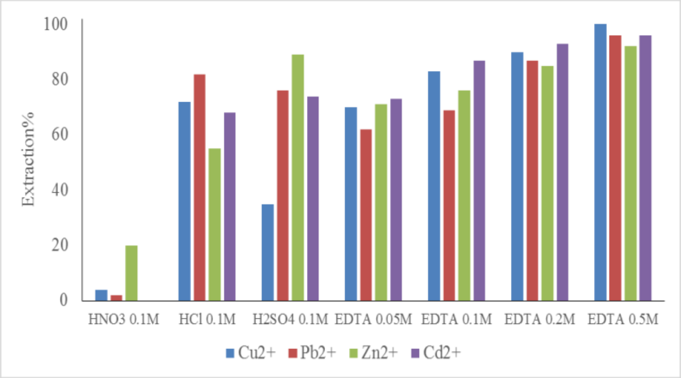


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Fig. 3. Effect of type of eluent on the recovery of 200 μg L^{-1} of Pb^{II}, Cd^{II}, Zn^{II} and Cu^{II}. Conditions: pH, 6; amount of adsorbent, 10.0 mg; sample volume, 50.0 mL, e xtraction time, 10min (n=3)

The effect of the eluent volume on the extraction of metal ions was also studied. Different volumes of eluent in the range of 3.0 to 5.0 mL were examined. According to the results shown in Fig. 4, 4.0 mL of EDTA (0.5 mol L^{-1}) was sufficient for quantitative recovery of analyte ions. Therefore, 4.0 mL of EDTA of 0.5 mol L^{-1} was selected as an eluent in further studies.

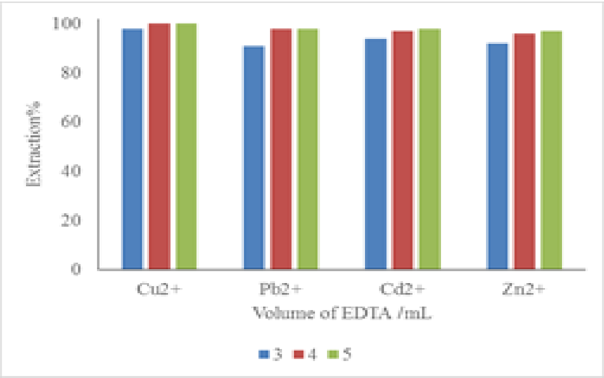

Fig. 4. Effect of volume of EDTA on the recovery of 200 μg L^{-1} of Pb^{II}, Cd^{II}, Zn^{II} and Cu^{II}. Conditions: pH, 6; sample volume, 50.0 mL; eluent, 4.0 mL of the EDTA (0.5 mol L^{-1}); e xtraction time, 10min (n=3)

3.3 Optimization of MNPs-Guanidine amount

In order to investigate the effect of the quantity of adsorbent on preconcentration of metal ions, various amounts of MNPs-Guanidine from 5.0 to 15.0 mg were used. The obtained results showed (Figure5) that percent of extraction increased with the increase of the adsorbent amounts from 5 to 15 mg indicate that the quantitative recovery (>95%) for cations was obtained when the amount of adsorbent was greater than 5.0 mg. Therefore, in the further experiments, 10.0 mg of adsorbent was applied.

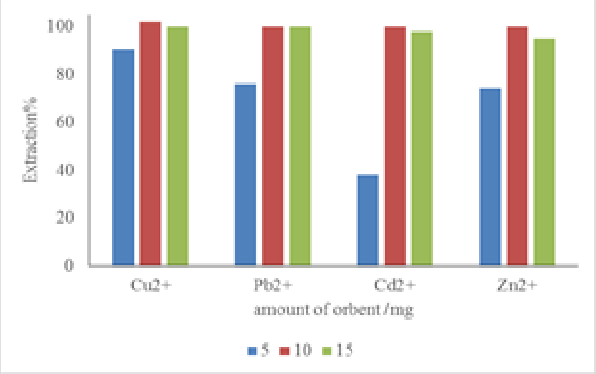

Fig. 5. Effect of amount of adsorbent on the recovery of 200 μg L^{-1} of Pb^{II}, Cd^{II}, Zn^{II} and Cu^{II}. Conditions: pH, 6; sample volume, 50.0 mL; eluent, 4.0 mL of the EDTA (0.5 mol L^{-1}); extraction time, 10min (n=3)

3.4 Effect of adsorption and desorption time

The ultrasonic times of adsorption and desorption analytes were also evaluated. The quantitative extraction of cations was obtained when ultrasonication time was greater than 10 min for adsorption and greater than 5 min for desorption. As, it was seen in Figure6, these ions can be extracted quantitatively by the MNPs-Guanidine when ultrasonication time was greater than 10 min for adsorption. Therefore, the optimum times of adsorption and desorption were 10 min and 5 min, respectively.

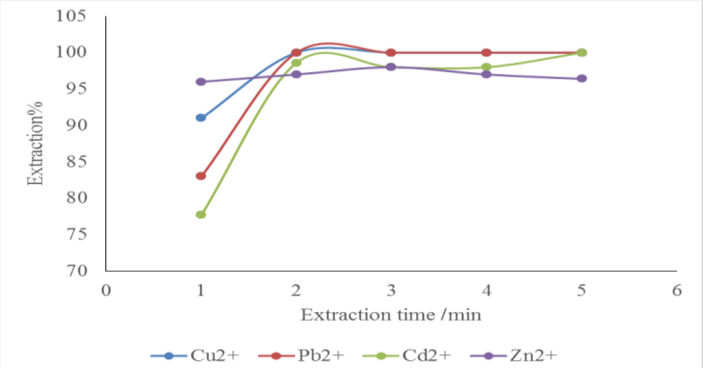

Fig. 6. Effect of extraction time on the recovery of 200 μg L^{-1} of Pb^{II}, Cd^{II}, Zn^{II} and Cu^{II}. Conditions: pH, 6; sample volume, 50 mL; eluent, 4.0 mL of EDTA (0.5 mol L^{-1}); extraction time, 10min (n=3)

3.5 The effect of the sample volume on extraction recovery

In order to obtain higher preconcentration factors, maximum applicable sample volume should be examined. For this purpose, the sample volumes of 50, 75, 100, 150, 200, 400, 500 and 1000 mL containing 10.0 μg of cations were studied according to the recommended procedure. The quantitative recoveries were achieved when the volume of sample was less than 400 mL. Thus, a sample volume of 400 mL was selected as the largest useable sample volume. Therefore, in this work, by using 4.0 mL of elution solution, a preconcentration factor 100 was obtained.

3.6 Effect of potentially interfering ions

In order to investigate selectivity of the method, the interference effect of different ions on the recovery of metal ions under the optimized conditions was evaluated. The concentration of diverse ions which resulted in an error ±5% in determination of 50.0 mL of 200 μg L^{-1} of Cu^{II}, Pb^{II}, Cd^{II} and Zn^{II} ions was considered as the tolerance limit. The results summarized in Table1 demonstrate that the method is relatively selective for determination metal ions.

Table 1. Effect of diverse ions on the determination of 200 μg L^{-1} of metal ions[a].

Interference species	Tolerable concentration			
	Ratio X/Pb^{II}	Ratio X/Zn^{II}	Ratio X/Cu^{II}	Ratio X/Cd^{II}
Na^+, K^+, NO_3^-	1000	1000	1000	1000
Mg^{2+}, Ca^{2+}	500	500	500	500
I^-, Br^-	500	500	500	500
Cl^-	200	200	200	200
CO_3^{2-} , SO_4^{2-}	200	200	200	200
Co^{2+} ,F^-	100	100	100	200
Fe^{2+}	50	50	50	50
Al^{3+}	4(10)[b]	4(10)[b]	20	10

[a] Conditions: pH, 6; amount of adsorbent, 10.0 mg; adsorption and desorption times, 10 and 5 min, respectively; eluent, 4.0 mL 0.5 mol L^{-1} EDTA

[b] The interference of Al^{3+} up to 10-fold was overcome by addition of 3.0 mL of 9.76×10^{-3} mol L^{-1} of NaF solution.

3.7 Sorption capacity

A batch method was used to calculate the sorption capacity. Langmuir isotherms were used to describe the absorption process at the solid-liquid interface which is represented by the following equation:

$$\frac{C}{q} = \frac{1}{kq_m} + \frac{C}{q_m}$$

where C (mg L^{-1}) is the equilibrium concentration, q (mg g^{-1}) is the amount of metal adsorbed per unit mass of adsorbent at equilibrium, q_m (mg g^{-1}) is the maximum amount of adsorption in mono layered adsorption systems and k (L mg^{-1}) is the langmuir constant, which can be considered as a measure of adsorption energy. A linear plot of C/q against C was applied to obtain the values of q_m and k from the slope and intercept of the plot.

In order to calculate the adsorption capacity, 3.0-10.0 mg L^{-1} of metal ions were added to 10.0 mg of adsorbent. The results indicated that the adsorption capacity of MNPs-guanidine for Lead, Copper, Zinc, and Cadmium are 15.2, 19.7, 12.2 and 13.6 mg g^{-1}, respectively.

3.8 Analytical characteristics of the proposed method

The analytical performance characteristics of the method are shown in Table2. Under the optimized conditions, linear calibration graphs were obtained for determination of Pb^{II}, Cu^{II}, Zn^{II} and Cd^{II}. The linear ranges were found to be 14-550, 40-600, 3.0-90 and 19.0 -200 for Cu^{II}, Pb^{II}, Cd^{II} and Zn^{II}, respectively. The limits of detection(LODs) were defined as $3S_b/m$ where m is the slope of calibration graph and S_b is the standard deviation of ten blank determinations for Pb^{II},

Cu^{II}, Zn^{II} and Cd^{II} were 11.8 μg L^{-1}, 4.78 μg L^{-1}, 7.6 μg $L^{-1}$and 1.08 μg L^{-1}, respectively. The recovery and repeatability of the method were also assessed by experiments performed on the similar solutions. Data in Table3 show that all cations are recovered more than 97% by the studied method. The repeatability of the method is good and relative standard deviation (RSD %) for five repeated experiments is less than 3.0% for all cations.

Table 2. Analytical characteristics of proposed method at the optimum conditions

Cation	Calibration curve equation	Linear dynamic range (μg L^{-1})	Correlation coefficient	Limit of detection (μg L^{-1})
Cu^{II}	A = 0.008C + 0.0033	14 - 550	0.994	4.78
Pb^{II}	A = 0.0028C + 0.0045	40 - 600	0.999	11.8
Cd^{II}	A = 0.02C - 0.002	3 - 90	0.997	1.08
Zn^{II}	A = 0.0052C + 0.003	19 - 200	0.995	7.6

Table3. Recovery and repeatability study

Recovery						Mean recovery ± standard deviation	Relative standard deviation (RSD%)
Cation	1	2	3	4	5		
Cu^{II}	100	100	99.6	100	99.8	99.88 ± 1.17	1.2
Pb^{II}	102	100	98.7	94.6	96	98.26 ± 2.98	3.0
Cd^{II}	95.1	95.5	98.7	100	97.5	97.36 ± 2.08	2.1
Zn^{II}	98.8	96	100	94	101	97.96 ± 2.89	2.9

3.9 Applications

In order to illustrate efficiency of the method, heavy metal content of different samples were determined by this method. Clear samples such as tap water to dirty samples such as municipality wastewater as well as high complex matrix sample such as Caspian Sea were selected for this purpose. Most of cations were found in these samples on the range of μg L^{-1} (Table4). Applicability of the method was evaluated by analyzing trace amounts of Pb, Cd, Zn and Cu in different water samples. The above mentioned samples were selected and the studied cations were added to them at two concentrations. The recoveries were calculated and compared to those obtained from samples prepared in distilled water. The results in Table4 show that in most samples, the deviation from ideal value (100%) is negligible. However this method can be useful for determination of heavy metals in most matrices at μg L^{-1} by using flame atomizer system.

Table 4. Comparative studies of obtained recoveries for cations in different water samples in comparison with those obtained from distilled water.

Real Sample	Added (μg L $^{-1}$)	Pb found (μg L $^{-1}$)	Recovery	Cu found (μg L $^{-1}$)	Recovery	Added (μg L $^{-1}$)	Cd found (μg L $^{-1}$)	Recovery	Zn found (μg L $^{-1}$)	Recovery
Caspian Sea	-	N.D	-	17.5±0.02	-	-	4.50±0.03	-	20.7±0.01	-
	100	99.5±0.02	99.5	114.09±0.01	96.6	25	29.1±0.03	98.4	45.1±0.03	97.6
	200	194.5±0.01	97.2	203.7±0.02	93.1	50	53.2±0.01	97.4	69.1±0.02	96.8
Municipality wastewater	-	32.0±0.01	-	42.5±0.04	-	-	3.3±0.01	-	40.5±0.01	-
	100	132.72±0.03	100.7	145.7±0.02	103.2	25	28.1±0.03	99.2	65.1±0.03	98.4
	200	230.26±0.02	99.1	238.5±0.3	98	50	52.8±0.04	99	88.9±0.10	96.8
Tap Water (sanandaj)	-	N.D.[a]	-	N.D	-	-	N.D	-	N.D	-
	100	98.3±0.2	98.3	99.1±0.04	99.1	25	23.9±0.05	95.6	24.1±0.03	96.4
	200	195.53±0.02	97.8	197.2±0.05	98.6	50	46.5±0.08	93	47.9±0.05	95.8
River water	-	N.D.	-	37.0±0.09	-	-	5.3±0.01	-	28.2±0.2	-
	100	99.2±0.01	99.2	135.6±0.05	98.6	25	29.7±0.2	97.6	52.1±0.10	96
	200	197.8±0.02	98.9	224.1±0.1	93.5	50	53.4±0.2	96.2	75.4±0.08	94.4
Well water	-	N.D	-	34.9±0.01	-	-	3.2±0.05	-	28.4±0.03	-
	-	N.D	-	17.5±0.02	-	-	4.50±0.03	-	20.7±0.01	-
	100	99.5±0.02	99.5	114.09±0.01	96.6	25	29.1±0.03	98.4	45.1±0.03	97.6

[a]Not detected

The primary advantage of the present method is that it can be used for simultaneous extraction four cations without need to a centrifugation step. A comparison with some of the previously reported works is also given in Table 5.

Table 5. Comparison results of some reported methods and present method.

Metal ions	PF[a]	Maximum (capacity mg g^{-1})	LOD µg L^{-1}	R.S.D%	Ref
Cu, Cd, Pb, Zn	80	-	0.16- 0.6	1-17	24
Cu, Pb, Cd, Zn	-	19.1, 116.0, 7.5, 8.8	1.0, 22.5, 1.1, 2.9	≤9	25
Pb, Cd, Ni, Zn	-	1.0, 3.9, 4.6, 6.2	7.2, 2.8, 4.3, 1.1	≤ 5	26
Cu, Ni, Zn	25	4.9, 4.8, 4.8	50, 40, 60	≤ 10	27
Cu, Pb, Cd, Ni	200 Cd(100)	15.4, 12.6, 6.1,	0.86, 0.58, 0.65, , 0.92	-	28
Cu	13	-	4.1	1.2	29
Cu, Pb, Cd, Zn	100	19.7, 15.2, 13.6, 12.2	4.78, 11.8, 1.08, 7.6	3.03	This work

[a] Preconcentration factor

4. Conclusion

In this study, magnetic Fe_3O_4 modified with guanidine has been applied for the preconcentration of four cations in water samples. It was found that this procedure was relatively selective, simple, fast, low cost and eco-friendly to nature with good preconcentration factor and wide linear dynamic range. As can be seen the present method has high capacity for simultaneous sorption of heavy metal ions as well as high preconcentration factor and good precision in comparison with other reported methods.

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